


Distribution and geochemical significance of trace elements in kerogens from Ediacaran–Lower Cambrian strata in South China

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Abstract Some trace elements (TEs), both bio-essential and redox-sensitive, are promising tracers of Earth's surface processes. As an essential sedimentary organic matter, kerogen may have inherited and retained the key TEs from organisms. In this study, the distribution of TEs in kerogens from two sections (Dongkangshang and Fengtan) in South China was analyzed to explore its biogeochemical significance during Ediacaran–Lower Cambrian. Compared with V and Zn, the relative concentrations of Co, Ni, Cu, and Mo were generally higher in kerogens than in the whole rocks. Enrichment of TEs in the kerogen was involved in the selective utilization of TEs by different organic precursors and the competition of sulfide in the depositional environment. The significant content of TEs in the kerogens from deep-water facies corresponded to a more negative $\delta^{13}\text{C}_{\text{ker}}$ as a result of the dominant taxa of chemoautotrophs with tremendous bioaccumulation potential for trace metals and the reduction conditions favorable for organic matter preservation. Furthermore, the content variations of trace elements in the kerogens coincided with the rise and fall of the Ediacaran biota, implying that the trace elements might have played an important role in early life evolution.

Keywords Trace elements · Kerogen · Ediacaran–Early Cambrian · Biogeochemical significance · South China

1 Introduction

Trace elements (TEs) can exist in sedimentary rocks combined with organic matter in addition to occurring in or adsorbed on minerals (Wu and Chu 2001; Han et al 2011). Some transition trace metals, such as nickel (Ni), copper (Cu), zinc (Zn), and molybdenum (Mo), are essential for the growth of organisms and are sensitive to the redox conditions of the sedimentary environment. These two features make them critical components of biogeochemical cycles in modern and past environments. At the molecular level, such elements function as active centers or structural factors in enzymes and are accumulated and stored by organisms through biochemical mechanisms (Morel et al. 2003). A portion of the assimilated TEs are usually discharged into the seawater during bacterial degradation processes, and the other parts are incorporated into the sediments during the deposition of the organic biomass (Morel and Price 2003; Sunda 2012). Besides the biotic processes, TEs in seawater could be adsorbed or complexed with organic matter through abiotic processes (Tribouillard et al. 2006), such as being chelated by $-\text{COOH}$, $-\text{OH}$, $-\text{SH}$, $-\text{NH}$, and other ligands of organic matter (Zhang et al. 2019). It has been widely recognized that organic matter plays a vital role in the formation of some metal deposits (Orberger et al. 2003; Coveney and Pašava 2004; Wen et al. 2006; Křibek et al. 2007; Shi et al. 2013), which also proves a close relationship between organic matter and TEs.

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Kerogen is an insoluble sedimentary organic matter with stable properties and complex structures. It has excellent potential in recording past biogeochemical cycles. A part of bio-essential trace elements, required explicitly by enzymes and proteins in organisms (Anbar 2008), will be deposited along with the non-degraded organic matter and eventually conserved in the kerogen. TEs occur in kerogen mainly in the three states: organic-bonded, occluded, or adsorbed. For instance, V and Ni occur typically in kerogen in the form of metalloporphyrin (Van Berkel et al. 1989). Se in kerogen may be organic-bonded or present as ultra-micro inclusions (Wen et al. 2003).

A variety of analytical methods have been conducted to determine the content of TEs in kerogen, including direct spectral quantitative determination (Yang 1982), instrumental neutron activation analysis (INAA, Mercer et al. 1993; Felitsyn and Morad 2002), atomic absorption spectrometry (AAS, Akinlua et al. 2007; Jegede et al. 2018), X-ray fluorescence spectrometry (XRF, Akinlua et al. 2010), and the most commonly used inductively coupled plasma mass spectrometry (ICP-MS, Wen and Qiu 1999; Pi et al. 2013; Adegoke et al. 2014; Deng et al. 2015; Guo et al. 2016; Xu et al. 2018). One of the difficulties in kerogen analysis derives primarily from the isolation procedure, in which some acid-resistant minerals, e.g., pyrite, rutile, and complex fluorides precipitate from the mixture of HCl–HF acids may persist. In addition, some submicron-nano mineral particles are physically combined with or wrapped in kerogen, which could induce the illusion that the TEs occurring in minerals are closely related to organic matter and have a particular impact on the statistical results. As a result, there is a high requirement for the purity of kerogen to analyze its trace element compositions.

Mercy et al. (1993) investigated the inorganic and organic associations of TEs in kerogen concentrates (not purified kerogen) of the New Albany shale. It has been found Ni and V had a substantial organic affinity, while Cr, Fe, Mn, Ti, Zr, and other elements were mainly present in mineral forms. There are differences in the trace element concentrations between kerogen and whole rock. Compared with the whole rock, kerogen is more enriched in V, Ni, Co, Cu, Ag, Tl, and Zn (Akinlua et al. 2010; Yang et al. 2015; Guo et al. 2016; Xu et al. 2018). The distribution of trace elements in kerogen has been applied for tracking the source of organic matter or identifying the paleo-redox environment in most studies (Pi et al. 2013; Adegoke et al. 2014; Deng et al. 2015; Guo et al. 2016; Jegede et al. 2018). For example, it was proposed that the geochemical fingerprint of trace elements in kerogen could be a promising approach for reconstructing the upper water column environment because kerogen was initially derived from organisms in the euphotic zone, less affected by

detrital material and hydrothermal input (Pi et al. 2013; Guo et al. 2016). From the uptake of marine organisms to sustain their life to the adsorption or complexation of organic matter, as well as the degradation and pyrolysis of organic matter in the sedimentary diagenetic stage, the migration and transformation of TEs are involved. Therefore it is expected that the distribution of TEs in kerogen could reflect the physical and chemical conditions of ancient marine associated with biological development. However, the enrichment process, occurrence state, and biogeochemical significance of TEs in kerogen have not been fully discussed, which deserves further exploration.

The continuous Ediacara–Cambrian sedimentary strata with diverse petrographic environments and abundant fossil records are well preserved in the Yangtze Block of South China. They provide an excellent opportunity to investigate the relationship between early life evolution and the marine environment. In this work, the trace element distribution in whole rocks and their corresponding kerogens from two sections (the Dongkanshang and Fengtan sections) of the Yangtze Block were analyzed using ICP-MS. The trace element data reported here were obtained from the kerogens with a carbon content greater than 60% and a loss on ignition (LOI) of more than 80%, with some kerogens having LOI above 98% (Table S1). That indicated only a tiny fraction of the acid-resistant minerals remained in the kerogens in this study. Co, Cu, Mo, Ni, V, and Zn are of particular interest as they are both redox-sensitive and bio-essential TEs. The focus is on the interactions among paleo-redox conditions, trace element concentrations and biological changes in the Ediacaran-early Cambrian ocean in South China.

2 Geological background

During the transition from Neoproterozoic to Phanerozoic, the Yangtze Block gradually evolved from a rifted basin to a passive continental margin basin after the recombination of the Laurasia and Gondwana supercontinents (Wang and Li 2003; Zhao et al. 2011; Jiang et al. 2011). Its basement is the Archean and Paleoproterozoic with medium–high metamorphism and the Mesoproterozoic with shallow metamorphism. Since the basement was formed, the Yangtze Block has become a relatively stable platform (Wang et al. 2007). Paleogeographic studies suggest three sedimentary facies: a carbonate shallow-water platform to the northwest, a siliceous and shaly deep-water basin to the southeast, and a transitional slope in between (Fig. 1A; Steiner et al. 2007; Jiang et al. 2012; Och et al. 2013; Jin et al. 2016).

The studied Dongkanshang and Fengtan sections are two outcrops on the upper Yangtze Block (Fig. 1A). The

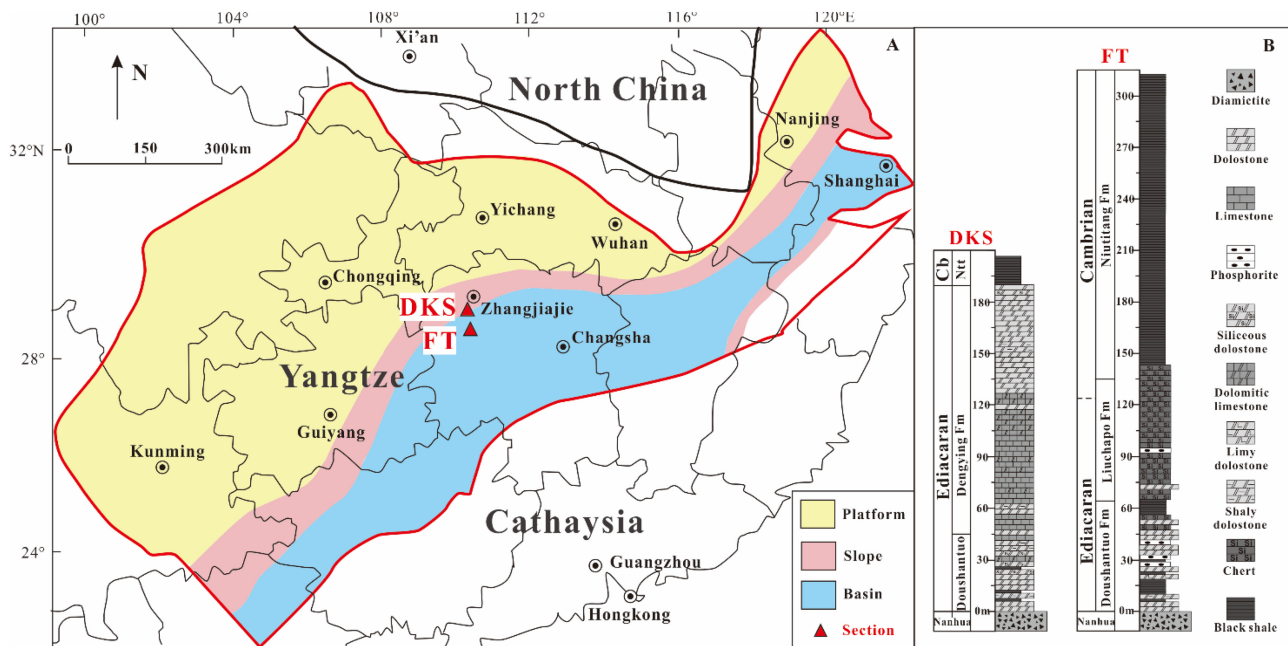


Fig. 1 Geological maps and stratigraphic columns. (A) A generalized paleogeographic map of the Yangtze Block during the Ediacaran–Early Cambrian (modified after Wang et al. 2017). The red triangles indicate the locations of the two studied sections. (B) Stratigraphic columns of the Dongkanshang and Fengtan sections. DKS: the Dongkanshang section; FT: the Fengtan section. Cb: Cambrian; Ntt: Niutitang

Dongkanshang section is in Yongshun County, Zhangjiajie City, and the Fengtan section is in Yuanling County, Huaihua City, Hunan Province. According to paleogeographic reconstruction, the Dongkanshang and Fengtan sections are deposited in slope and basinal settings, respectively. The slope Dongkanshang section is 220 m thick, consisting of the Ediacaran Doushantuo, Dengying, and the Cambrian Niutitang Formations in ascending order. The basinal Fengtan section is above 300 m thick, including the Doushantuo, Liuchapo, and Niutitang Formations (Fig. 1B). The Dengying and the Liuchapo Formations were regarded as time-equivalent traditionally. However, further geochronological studies showed that the Liuchapo Formation is a diachronous stratigraphic unit spanning the Ediacaran–Cambrian boundary (Wang et al. 2012; Chen et al. 2015; Lan et al. 2017). U–Pb zircon dating from volcanic ash beds within the Doushantuo Formation indicated that its deposition occurred between 635.2 ± 0.6 and 551.0 ± 0.7 Ma (Condon et al. 2005; Zhang et al. 2005; Chen et al. 2015), and the age of the Precambrian–Cambrian boundary has been dated to 541.0 ± 1.0 Ma (Chen et al. 2015).

The Ediacaran–Lower Cambrian strata in South China overlie the glacial diamictites of the Nanhua System (Fig. 1B). At the platform in the Yangtze Gorges area, the Ediacaran Doushantuo Formation is divided into four lithostratigraphic members (Members I–IV). Member I refers to the cap carbonate at the bottom of the Doushantuo Formation. Member II consists of interbedded shale and

limestone that contain abundant acanthomorphic acritarchs. Member III is composed of thin- to thick-bedded dolostone and limestone. Member IV refers to the organic-rich black shales at the top of the Doushantuo Formation (Wang et al. 2016). The lithology of the platform margin, slope, and basin facies change with the sedimentary facies. In this study, sedimentary rocks in the slope Dongkanshang section consist of dolostone, limestone, and a few mudstones. The lithologies of the basinal Fengtan section are different from those of the Dongkanshang section. As the Fengtan section was deposited in the deeper water, the content of carbonate decreased while the siliceous component increased. There are cap dolostone and black shale at the lower part, dolostone and phosphorite at the middle part, and interbedded dolostone and chert at the upper part of the Doushantuo Formation. The Liuchapo Formation is a continuous siliceous deposition. During Early Cambrian, the Niutitang Formation witnessed a huge deposit of black shale. The small shelly fossils represent an important biostratigraphic tool for correlating the Lower Cambrian strata worldwide (Steiner et al. 2007).

3 Methods and experiments

19 sedimentary rock samples from the Dongkanshang Sect. (6 from the Doushantuo Formation, 9 from the Dengying Formation, and 4 from the bottom of the Niutitang Formation) and 28 sedimentary rock samples from the

Fengtang Sect. (16 from the Doushantuo Formation, 9 from the Liuchapo Formation, and 5 from the Niutitang Formation) were selected for the analyses of TEs of the whole rocks and their corresponding kerogens. The total organic carbon (TOC) content of the whole rocks was analyzed on an Eltra CS-800 carbon–sulfur determinator to ensure that an adequate amount of kerogen could be isolated for the trace element analysis. Any weathered surfaces, post-depositional veins, and visible pyrite crystals were carefully removed. Selected rock pieces were then pulverized (200 mesh) before geochemical analyses.

3.1 Analysis of trace elements of whole rock

The trace element concentrations of the whole rocks were accomplished at the ALS Laboratory Group's Mineral Division, ALS Chemex, in Guangzhou, China. The powdered rock samples were digested with HNO_3 – HClO_4 – HF – HCl mixed acids, and organic-rich samples were combusted at 750 °C before digestion. Trace element concentrations were determined by an Agilent 7700 × ICP-MS combined with an Agilent VISTA ICP-AES. The relative deviation and the relative error of elemental concentration are less than 10%.

3.2 Analyses of C, H, and N composition and trace elements of kerogen

The isolation of kerogen was performed following Fu and Qin (1995). About 50 g powdered rock sample was treated repeatedly with dilute HCl and HF to remove carbonate and silicate minerals. The residue (i.e., kerogen) was then washed with deionized water until a neutral state was attained and dried.

The elemental analysis of C, H, and N of kerogen was conducted on a Vario EL III element analyzer at the State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry. Each sample was analyzed at least twice, and the average value of the two analysis results with good parallelism was taken. To minimize the interference of mineral impurities (such as pyrite or other acid-insoluble minerals and newly formed fluorides), the kerogens with a carbon content greater than 60% were selected for trace element analysis.

The trace element analyses of the kerogens were performed at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry. Kerogen was first combusted in a muffle oven at 650 °C for 4 h before digestion with an HNO_3 – HF – HClO_4 mixture. Elemental analysis was carried out on an Elan 6000 ICP-MS, and the results were calibrated by the loss ratio after combustion.

4 Results and discussion

4.1 Distribution of trace elements in kerogens

In this study, the distribution of several TEs in the Ediacaran–Lower Cambrian kerogens from the two sections was similar. Among the interested TEs, Ni (4.20–204.03 µg/g for the Dongkangshang section, 8.11–929.14 µg/g for the Fengtan section) was the most abundant trace element in the kerogens, followed by Cu (2.56–80.92 µg/g for the Dongkangshang section, 7.74–692.98 µg/g for the Fengtan section), V (1.51–236.17 µg/g for the Dongkangshang section, 0.80–201.83 µg/g for the Fengtan section), Mo (0.63–39.64 µg/g for the Dongkangshang section, 0.06–251.83 µg/g for the Fengtan section), Co (0.10–32.32 µg/g for the Dongkangshang section, 0.19–90.22 µg/g for the Fengtan section), and Zn (2.22–15.34 µg/g for the Dongkangshang section, 0.82–66.11 µg/g for the Fengtan section) (Table S1). Generally, the trace element concentrations of kerogens from the Fengtan section of deep-water basin facies were higher than that in the Dongkangshang section of shallow-water slope facies. Ni and Cu were the most enriched in kerogens, verifying the close association between Ni, Cu, and organic matter, making them available as effective proxies of organic carbon sinking flux and paleoproductivity (Tribouillard et al. 2006).

The enrichment factors (EF represents the ratio of trace element concentration of kerogen to that of whole rock) of V, Co, Ni, Cu, Zn, and Mo in kerogen relative to whole rock are displayed in Table S2 and Fig. 2. In the Dongkangshang section, most samples exhibited more enrichment of kerogens than whole rocks for Ni ($\text{EF} > 1$) and more enrichment of whole rocks than kerogens for Zn ($\text{EF} < 1$). At the same time, the enrichment of kerogens relative to whole rocks for V, Co, Cu, and Mo in the Ediacaran and Cambrian samples differed. The Ediacaran kerogens exhibited more enriched in these TEs than the whole rocks, and the Cambrian rocks revealed more enriched in these TEs than their corresponding kerogens (Fig. 2A). This might be due to the apparent changes in the biotype or depositional environment when the Dongkangshang section was deposited during the Ediacaran–Cambrian transition. For the Fengtan section, the EF values of the Ediacaran and Cambrian samples were similar (Fig. 2B), and the kerogens were more enriched in Ni, Cu, and Mo than the whole rocks, while the whole rocks were more enriched in V and Zn than the kerogens. Although V and Zn can be bio-accumulated and delivered to the sediments as organometallic compounds, the concentration of V and Zn in kerogen is not higher than that in the whole

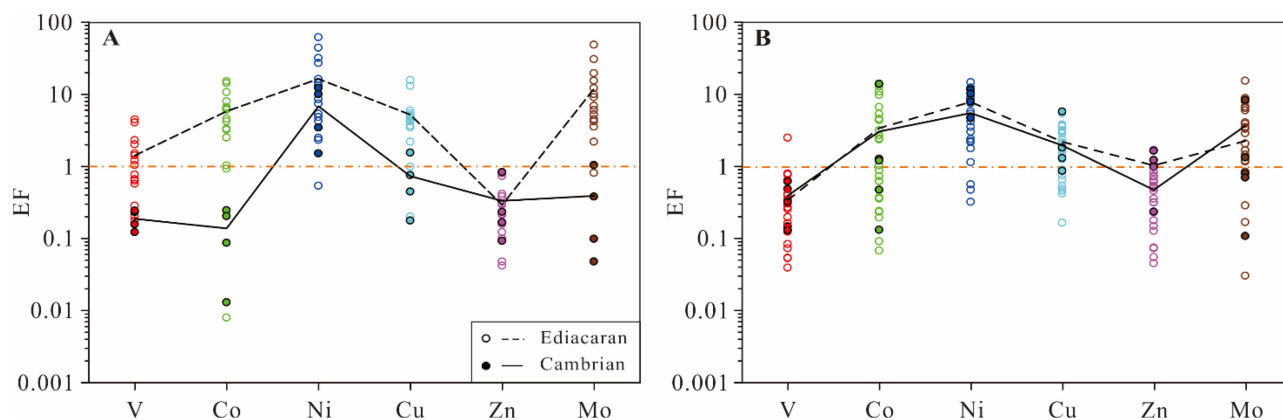


Fig. 2 The EF values of V, Co, Ni, Cu, Zn, and Mo for the Dongkangshang section (A) and Fengtan section (B). The dots represent the EF values, and the lines connect the average EF values

rock, indicating that the presence of V and Zn associated with organic matter is limited. Because V prefers to be substituted for Al in the octahedral sites of clay minerals rather than forming complexes with organic matter (Breit and wanty 1991; Huang et al. 2015; Awan et al. 2021). Another interpretation for the lower contents of V and Zn in the kerogens compared to the whole rocks is that V and Zn are prone to be remobilized from kerogens during degradation and pyrolysis compared with Co, Cu, Ni, and Mo (Algeo and Maynard 2004).

The stratigraphic variations of trace element concentrations of the kerogens were consistent with those of the whole rocks (Figs. 3, 4). In the Dongkangshang section, the concentrations of Mo, V, Cu, Ni, and Zn were higher in the Doushantuo Formation, then decreased slightly in the Dengying Formation, and increased in the Niutitang Formation. The concentration of Co was higher in the Doushantuo Formation, then gradually decreased, and it was at a reduced level in the Niutitang Formation. In the

Fengtan section, the concentrations of V, Co, Cu, Ni, Zn, and Mo increased from the Doushantuo Formation to the Liuchapo Formation and declined at the Niutitang Formation. The changes in the trace element concentration of kerogens were not synchronous with the changes in TOC of the whole rocks (Figs. 3, 4, 5), indicating that the enrichment of trace elements in kerogen was not only constrained by the content of organic matter of the sedimentary rock.

4.2 Possible controls on the distribution of trace elements in kerogen

The geochemical genesis of trace elements in kerogen involves both primary and secondary processes. Primary processes include the uptake and binding of trace elements by the biological precursors of kerogen in seawater or at the sedimentary interface. In contrast, secondary processes are the mobilization and migration of trace elements through kerogen thermal or biological degradation. Thus,

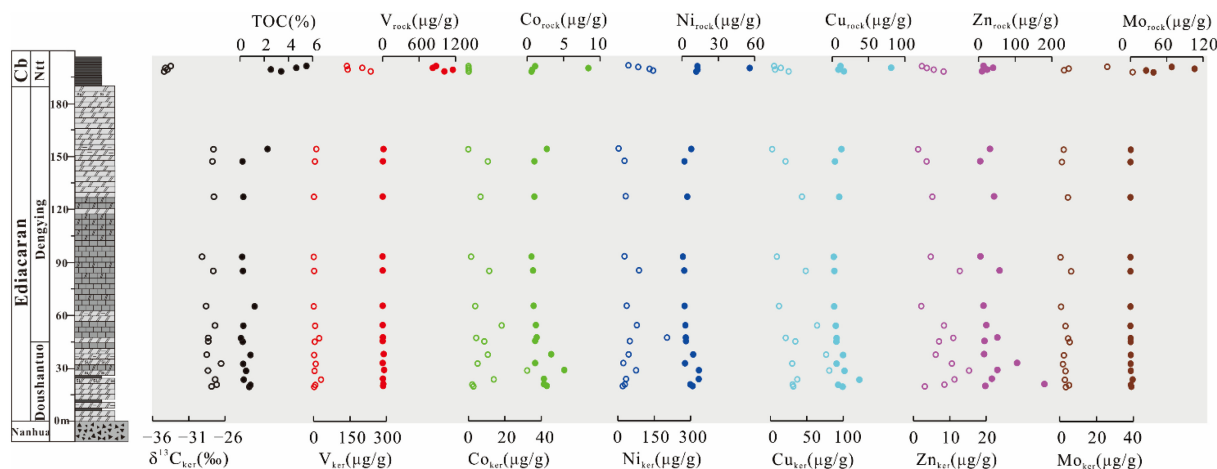


Fig. 3 Stratigraphic profiles of $\delta^{13}\text{C}_{\text{ker}}$, TOC, concentration of V, Co, Ni, Cu, Zn, and Mo of kerogens (hollow dots) and whole rocks (solid dots) for the Dongkangshang section. $\delta^{13}\text{C}_{\text{ker}}$ data are from Fang et al. (2019)

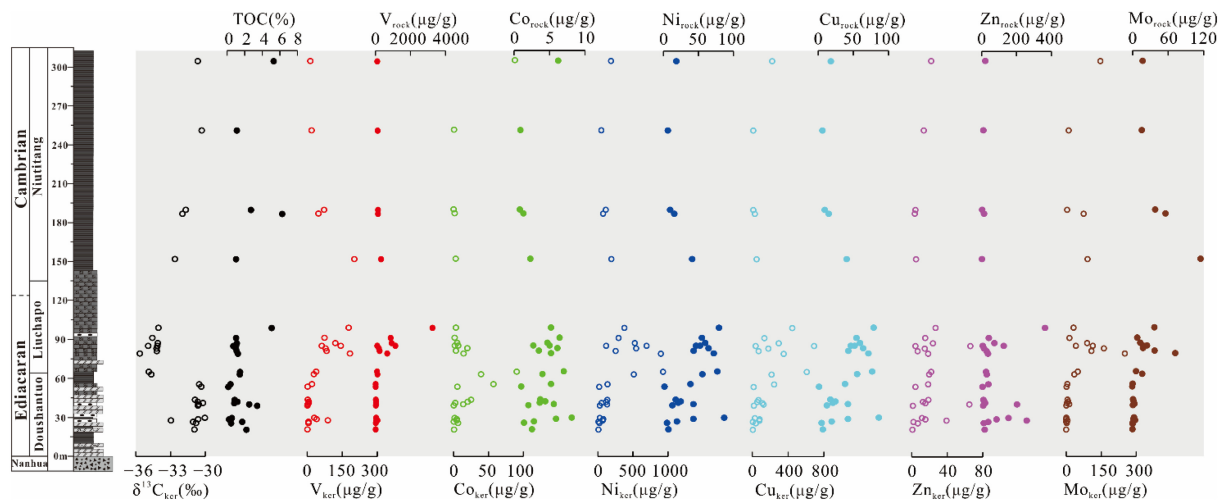


Fig. 4 Stratigraphic profiles of $\delta^{13}\text{C}_{\text{ker}}$, TOC, concentration of V, Co, Ni, Cu, Zn, and Mo of kerogens (hollow dots) and whole rocks (solid dots) for the Fengtan section. $\delta^{13}\text{C}_{\text{ker}}$ data are from Fang et al. (2019)

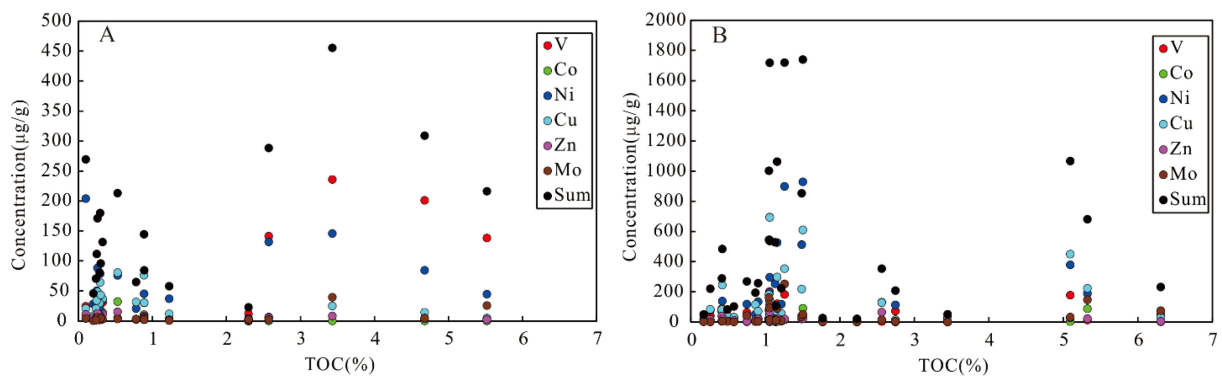


Fig. 5 Crossplots of the concentration of V, Co, Ni, Cu, Zn, Mo and their overall content of kerogens vs. TOC content of whole rocks for the Dongkangshang section (A) and Fengtan section (B)

the trace element composition of kerogen could be related to many processes, which include absorption of the biological precursors, interaction with bottom seawater, hydrothermal venting during degradation and maturation of the organic matter, competition with sulfides during diagenesis, and metamorphism of the hosting rocks. Based on the biogeochemical cycles of trace elements, the influences of biological precursors, depositional environment, and post-depositional processes on the trace element distribution in kerogen are considered.

4.2.1 Biological precursors

Biologically, some TEs play an essential role in the enzymatic reactions of photosynthesis, respiration, nitrogen fixation, and other metabolisms of organisms (Robbins et al. 2016; Morel et al. 2020). In turn, marine organisms play a crucial role in the cycling of trace elements by uptake, metabolizing, and altering the species of these TEs

in seawater. The process of trace element uptake by cells involves (1) binding to active organic ligands on the cell surface through adsorption, (2) assimilation of trace elements to form metalloenzymes for the requirement of life, and (3) production of extracellular ligands binding trace elements to alter their bioavailability (Shi et al. 2013; Fein 2017; Bishop et al. 2019). Biological uptake usually results in higher intracellular trace element concentrations than those in the surrounding seawater (Zhang et al. 2019), as well as low concentrations of these nutrient TEs in the euphotic zone (Morel and Price 2003; Sunda 2012). Plankton or microorganisms in the ocean have considerable adsorption of nutrient TEs such as Zn, Cu, and Ni, which is one of the important ways to deliver trace metals from the euphotic zone to the deep water and sediments (Playter et al. 2017; Bishop et al. 2019; Baumgartner et al. 2020). Nonetheless, trace elemental composition varies among species (Ho et al. 2003; Morel et al. 2003; Dupont et al. 2006).

The spatiotemporal heterogeneous $\delta^{13}\text{C}_{\text{ker}}$ of the Ediacaran–Cambrian strata in South China reflects a difference in dominant taxa at different water depths and in different depositional environments (Ader et al. 2009; Jiang et al. 2012; Fang et al. 2019). The higher $\delta^{13}\text{C}_{\text{ker}}$ values ($> -30\text{‰}$) in the shallow water reflect the isotopic fractionation dominated by photosynthesis, while the lower $\delta^{13}\text{C}_{\text{ker}}$ values ($< -32\text{‰}$) in the deep water reflect a contribution of chemoautotrophic or methanotrophic biomass to the organic matter in the anoxic environment (Wang et al. 2014). Negative excursions of $\delta^{13}\text{C}_{\text{ker}}$ occurred at the base of the Niutitang Formation in the Dongkanshang section and the bottom of the Liuchapo Formation in the Fengtan section (Figs. 3, 4), accompanied by a lithofacies transition from shallow-water dolomite to deep-water siliciclastic rock and black shale, which implied an increase in water depth and the transgression events (Zhang et al. 2020). The extreme negative $\delta^{13}\text{C}_{\text{ker}}$ values (*ca.* -34‰) might be due to chemoautotrophic or methanotrophic microorganisms as the main source of sedimentary organic matter under anoxic conditions in deep water. With the deepening of the water column and the change in the dominant taxa indicated by the negative $\delta^{13}\text{C}_{\text{ker}}$ anomalies, the concentrations of some bio-essential TEs in the kerogens were significantly higher, especially V, Ni, and Mo (Figs. 3, 4). The possible interpretation is the greater bioaccumulation potential of trace metals by chemoautotrophic organisms in the deep water (Demina 2015), resulting in the uptake and storage of more TEs. Moreover, the anoxic conditions in the deep water facilitated the preservation of organic matter. Thus, more TEs associated with kerogens were conserved.

4.2.2 Depositional environment

Essential trace elements in the ocean exist as different chemical species, which strongly influences their biological uptake and biogeochemical cycling. They occur in different oxidation states, which have different solubilities, binding strengths with organic ligands, ligand exchange kinetics, and bioavailabilities. Consequently, the redox condition has a major influence on their chemical behavior, biological uptake, and biogeochemical cycling (Sunda 2012). During deposition, the remains of organisms are degraded by microorganisms releasing a portion of TEs into the seawater to re-participate in the biogeochemical cycle or be captured by pyrite in a reducing environment (Tribovillard et al. 2006). In addition to the biotic accumulation of TEs in organisms, TEs will be associated with organic matter through physical adsorption or chemical binding (Swaine et al. 1990; Zhang et al. 2019), which is another contribution to TEs in kerogen.

Eh and pH of the sedimentary environment can alter the ability of TEs to combine with organic matter. At low pH, hydrogen ion has a high affinity and participates in the competition between complexation sites in organic matter and metal ions, such as the protonation of amino and carboxyl groups, which weakens the complexation of organic matter with metal ions. At high pH, the dissociation of acidic oxygen-containing functional groups in organic matter will increase, making more negative electricity in organic matter and increasing its complexing ability to metal ions (Bishop et al. 2019). V-organic complexes, for example, are more stable at high Eh and near neutral to alkaline conditions (Gustafsson 2019). In addition, the different redox conditions will change the occurrence state of TEs. Under low Eh conditions, although the organic matter is well preserved, the presence of sulfide will significantly impact the combination of TEs and organic matter. For example, Helza and Vollicek (2019) believe that the enrichment of Mo in organic-rich sedimentary rocks does not come from the assimilation of organisms or the combination of organic functional groups. Specifically, MoO_4^{2-} in water is transformed into $\text{MoO}_{4-x}\text{S}_x^{2-}$ precipitation through microbial-mediated sulfate reduction and the role of organic matter is restricted under the euxinic condition.

In the Dongkanshang section, Mo concentrations of the whole rocks in the Niutitang Formation are higher than that of the kerogens, contrary to the Precambrian samples (Fig. 2), which might be related to the variation of redox conditions because Mo is a trace element susceptible to redox conditions. It's demonstrated that the Ediacaran in the Dongkanshang section was predominantly deposited in oxic-suboxic conditions with episodic anoxic conditions, while the Niutitang Formation was deposited in anoxic-euxinic conditions (Fang et al. 2019). Mo mainly exists in organic matter in non-euxinic conditions, while it tends to occur as sulfide under euxinic conditions (Algeo and Maynard 2004). In addition, the euxinic conditions are unfavorable to the survival of organisms and limit the assimilation of Mo by organisms (Anbar and Knoll 2002). Together, these factors caused the whole rocks of the Niutitang Formation to be more enriched in Mo than the kerogens. The concentrations of Cu, Co, V, and Zn in the whole rocks were higher than the kerogens of the Niutitang Formation in the Dongkanshang section might likewise be owing to the critical role of the euxinic conditions in the enrichment of these metals (Guo et al. 2016). In the Fengtan section, the enrichment of these TEs in kerogens relative to the whole rocks in the Ediacaran was the same as in the Cambrian, which reflects a relative stable redox environment in the deep water during the Ediacaran–Cambrian transition, mainly under anoxic conditions (Fang et al. 2019). In this case, the distribution of TEs in kerogen

was more influenced by element properties and biological development.

4.2.3 Post-depositional processes

Post-depositional processes such as burial diagenesis and thermal maturation may cause the mobilization of elements associated with organic matter (Ardakani et al. 2016). The chemical composition of the primary organic matter will be altered by thermal maturation through the loss of functional groups, generation of hydrocarbons, and molecular reorganization (Seewald 2003). Theoretically, the organic fluids produced in the pyrolysis of organic matter lead to the migration of some TEs, but in practice, this migration is restricted by the binding strength of organic matter and elements and the oil–gas migration channel (e.g., microfracture size) (Chen and Wang 2000). For example, except for V and Ni, the contents of TEs in crude oil and bitumen are relatively low (Filby et al. 1994; Huang et al. 2015). Dickson et al. (2019) attributed the increase in Mo, Zn and Cd concentrations in residual rocks with the rise of thermal maturity to the mass loss of organic fluids from the kerogen pyrolysis, and the concentration of Mo, Zn, and Cd in these organic fluids was low. In other words, maturation has little impact on the trace element content in kerogen (Mongenot et al. 1996; Ni et al. 2018). Paradoxically at the molecular level, the molecular structure of kerogen changes with the increasing maturity: cleavage of aliphatic structures, shedding of oxygen-containing functional groups, and condensation of aromatic structures, which may lead to a reduction of organically bound TEs. For example, Akinlua et al. (2007) and Adegoke (2014) discovered that the concentration of trace metal elements in kerogen decreased with the increase of maturity in organic-enriched intervals, but this trend was not evident in low organic matter strata. The effect of thermal maturity on the distribution of trace elements in kerogen is not well understood. Nevertheless, the effect of maturity is unlikely to have an adverse impact on the paleoenvironment interpretation in a particular stratigraphic sequence with a common burial history on a limited spatial scale (e.g., in the same basin).

4.3 Geochemical implications of trace elements in kerogen

4.3.1 Organic accumulation mechanism

TEs are often used as proxies for reconstructing the productivity and redox conditions of ancient marine sediments. For example, Ni is delivered to the sediments mainly in association with organic matter, less affected by the change from anoxic to sulfide environments (Algeo and

Maynard 2004). This property makes it useful as a paleo-productivity proxy (Tribovillard et al. 2006). Ni in kerogen can more precisely indicate the paleoproductivity than in the whole rock because the detritus- or hydrothermal-sourced Ni is excluded (Guo et al. 2016). Also, the authigenic enrichment of V and U under reducing conditions makes $V/(V + Ni)$ and Th/U ratios serve as paleo-redox proxies in traditional ways (Jones and Manning 1994). Although it has been suggested that the redox threshold indicated by trace element indicators may change under different sedimentary systems (Algeo and Liu 2020; Algeo and Li 2020), the change of these trace element ratios on the profile should be able to identify the trend of redox changes. These ratios decreased with the increased oxidation of the depositional environment.

The range and variation of the Th/U ratios of the kerogens and whole rocks were consistent (Table S2, Fig. 6). However, the $V/(V + Ni)$ ratios of the kerogens were lower than that of the whole rocks due to the more significant enrichment of Ni in kerogen than V (Fig. 6). An anoxic bottom water environment was indicated by the low Th/U and high $V/(V + Ni)$ ratios of the whole rocks. Based on the variations of the Th/U and $V/(V + Ni)$ ratios, a gradual increase in anoxia from the Doushantuo Formation to the Dengying/Liuchapo Formation and a gradual tendency to oxidation to the early Cambrian were concluded. The rocks with high TOC contents from the Ediacaran–Lower Cambrian strata of the Dongkangshang and Fengtan sections had $V/(V + Ni)$ ratios ranging from 0.8 to 1, while the Ni concentration in their corresponding kerogens was not high ($< 400 \mu\text{g/g}$) (Fig. 7), suggesting that anoxic conditions rather than productivity exerted a major control on the accumulation of organic matter. However, the effect of productivity could not be easily ignored as those rocks from the Fengtan section with high Ni concentration of kerogen ($> 400 \mu\text{g/g}$) did not have low TOC contents (about 1%). According to Fig. 7, the organic matter accumulation in the Dongkangshang section was mainly controlled by anoxic conditions. In contrast, anoxic conditions and paleoproductivity jointly constrained the organic accumulation in the Fengtan section.

4.3.2 Seawater chemistry and biological evolution

It is challenging to measure trace element compositions in the paleo-ocean directly. It is believed that iron formation, black shale, and sedimentary pyrite could provide unique insights into variations in the trace element concentrations in ancient marine at geological time scales (Konhauser et al. 2009; Scott et al. 2013; Robbins et al. 2013, 2016; Large et al. 2014, 2015). Variations in trace elements in the paleo-ocean on geological time scales correlate with the oxygen level of the atmosphere–ocean system and

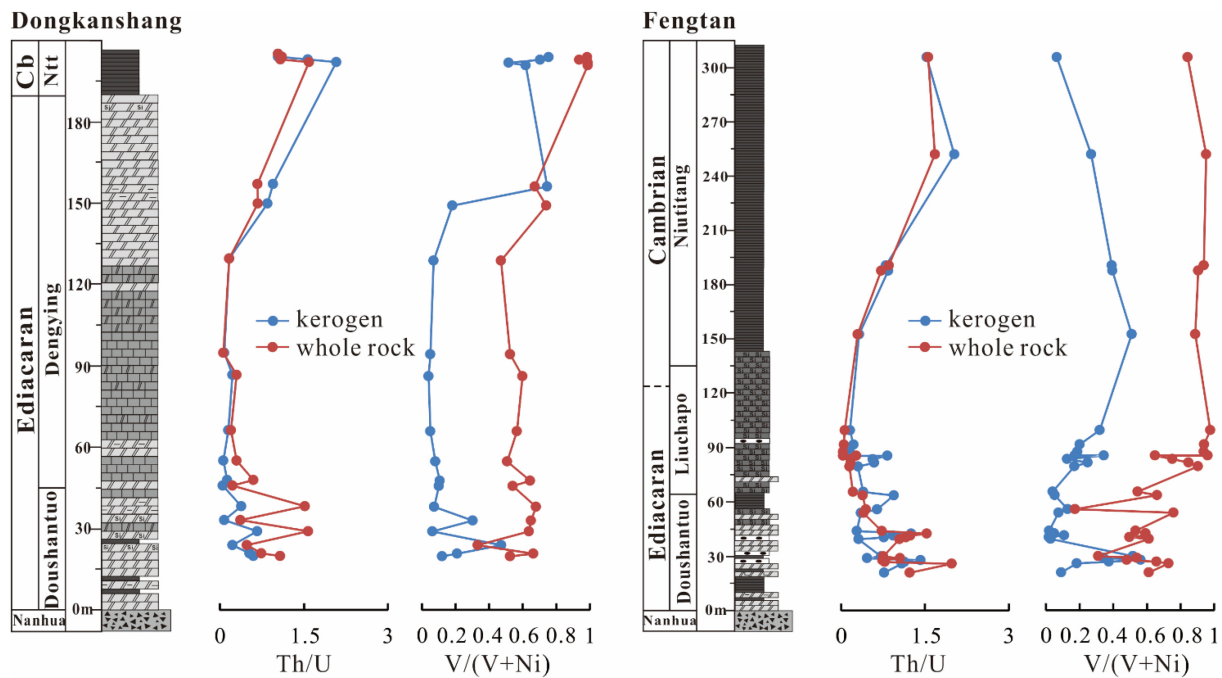


Fig. 6 The Th/U and V/(V + Ni) ratios of the kerogens and the whole rocks

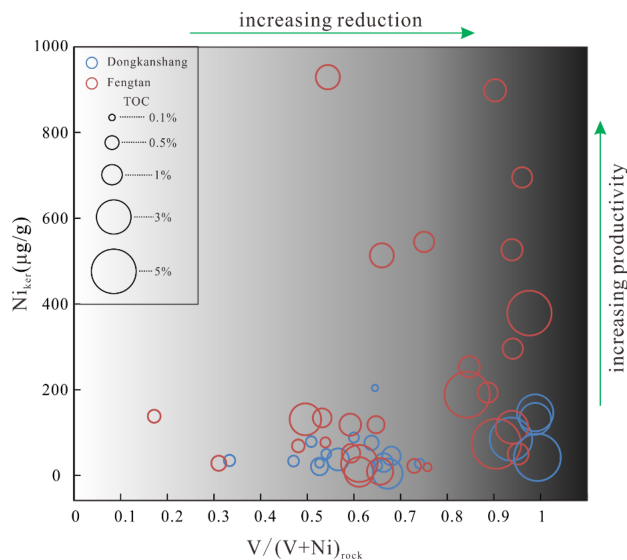


Fig. 7 Crossplot of V/(V + Ni) of the whole rocks and Ni concentration of kerogens (the size of the circles indicates the level of TOC content)

correspond to various stages of biological evolution during geologically critical periods. The nutrient-rich oceans fostered key evolutionary events, while nutrient-poor oceans encompass several major mass extinction events (Large et al. 2015).

The Ediacaran–Cambrian transition marks pivotal biological revolutions, including the emergence and extinction of Ediacaran biota and the subsequent well-known

Cambrian Explosion. The Ediacaran biota that lived between *ca.* 575–541 million years ago is an enigmatic group of soft-bodied organisms representing the first radiation of large, morphologically complex multicellular eukaryotes. The first recognition of Ediacaran-type fossils was in eastern Newfoundland by Billings (1872). These remarkable fossils have since been found in Western Australia (Sprigg 1949), Northwestern Canada (Hofmann et al. 1990), and other regions. The Doushantuo, Lantian, Dengying, and Liuchapo Formations in South China also record abundant Ediacaran taxa, such as Lantian Biota, Weng'an Biota, Miaohe Biota, Wulingshan Biota, and Xilongxia Biota, which comprise acanthomorphic acritarchs, animal embryos, multicellular algae, and biomineralizing animals (McFadden et al. 2009; Zhu 2010; Chen et al. 2015). The Ediacaran biota largely disappeared across the Precambrian–Cambrian boundary and was replaced by rapidly evolving metazoan in Cambrian Explosion (Narbonne 2005; Shu 2009; Darroch et al. 2018).

In the Dongkanshang and Fengtan sections, the fluctuating concentrations of Co, Cu, Ni, Mo, V, and Zn of the kerogens increased from the middle of the Doushantuo Formation. They reached high levels near the Doushantuo–Dengying/Liuchapo Formations boundary, with a decreasing trend toward the top of the Ediacaran and the Lower Cambrian Niutitang Formation (Figs. 3, 4). These geochemical changes, which reflect the disturbances in the seawater chemistry, may probably have a critical effect on the evolution of the Ediacaran biota. During the Neoproterozoic Oxidation Event, increased atmospheric oxygen

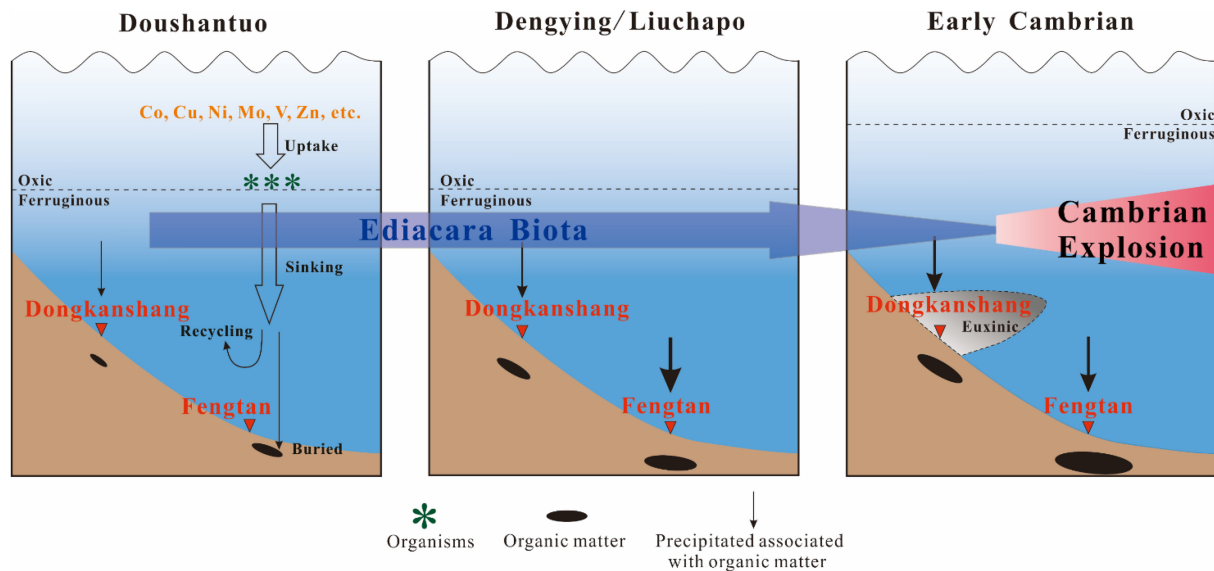


Fig. 8 A pattern of geochemical cycling and evolution of TEs associated with the development of the Ediacaran biota during the Ediacaran–Early Cambrian in South China. The size of the arrows indicates the relative sinking flux of TEs associated with organic matter

levels promoted continental weathering and increased trace element input to the oceans. Thus, there was an overall trend of increasing some nutrient TEs in the oceans during the Late Neoproterozoic (Large et al. 2015; Mukherjee and Large 2020). The increase of TEs accompanied by the gradual oxidation contributed to the establishment of aerobic metabolism and complex ecosystems. After the rise of the Ediacaran biota, the demand for organisms for nutrient TEs increased. The trace elements they assimilated into their bodies settled on the seafloor, part of which was released from the organic matter for recycling due to microbial degradation, and the other part was delivered to the sediment in association with organic matter and was finally preserved in the kerogen (Fig. 8; Awan et al. 2021). However, the constant anoxic or euxinic bottom water may have drawdown the trace element inventory in the seawater through the elevated burial flux of TEs associated with organic matter or sulfide (Algeo 2004) leading to a TE-depleted ocean near the Ediacaran–Cambrian boundary. And that might be one of the induced mechanisms of the extinction of the Ediacaran biota. This seawater chemistry and ecosystem adjustment could also prepare for the Cambrian Explosion (Han et al. 2018). Incredibly complex interactions among geological events, seawater chemistry, and biological evolution require more comprehensive and interdisciplinary investigations.

5 Conclusions

- (1) The kerogens from Ediacaran–Lower Cambrian were more enriched in Co, Cu, Mo, and Ni while the

concentrations of V and Zn were higher in the whole rocks. The trace element enrichment of kerogen relative to the whole rock varied in different depositional settings before and after the Cambrian.

- (2) The dominant chemoautotrophs in deep water with a greater bioaccumulation potential of trace metals and the reduction conditions conducive to preserving organic matter could induce a link between the enhanced TEs in kerogen and the negative $\delta^{13}\text{C}_{\text{ker}}$ excursions.
- (3) The variation of Th/U and V/(V + Ni) ratios of the whole rocks and kerogens combined with the Ni content of the kerogens indicated that the organic matter accumulation in the Ediacaran–Lower Cambrian of the Dongkanshang section was mainly controlled by anoxic conditions. Contrarily, the organic matter enrichment in the Fengtan section was jointly influenced by anoxic conditions and paleoproductivity.
- (4) The dramatic environmental changes inferred from the large $\delta^{13}\text{C}_{\text{ker}}$ excursions and drawdown of trace element concentration occurred coincidentally with the biological changes across the Precambrian–Cambrian boundary, which confirmed the changes in the marine environment were intimately linked to the biological evolutions.

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Declarations

Conflict of interest The authors state that there is no conflict of interest.

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